PCBs and Pesticides in Surface Water by XAD-2 Resin Extraction

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1.0 Application

1.1 This method is used to determine congener specific PCB and pesticide concentrations at trace levels in surface water. A multi-plate filtration system for collection of particulates, and an XAD-2 resin column for collection of dissolved PCBs is used. Water volumes of 80 L to 160 L can be analyzed by this method.

1.2 The following limits of detection (method detection limits) were determined for the resin ("dissolved") PCBs and the filters ("particulate") PCBs for sample sizes of 80 L and 160 L:

BZ # (1)	80 L		160 L	
	LOD (MDL) ng/L	LOQ ng/L	LOD (MDL) ng/L	LOQ ng/L
#3	0.43	1.4	0.22	0.72
#4/10	0.050	0.17	0.025	0.083
#7/9	0.011	0.037	0.0055	0.018
#6	0.022	0.073	0.011	0.037
#8/5	0.049	0.16	0.024	0.080
#19	0.0070	0.023	0.0035	0.012
#18	0.014	0.047	0.0070	0.023
#15/17	0.030	0.10	0.015	0.050
#24/27	0.0070	0.023	0.0035	0.012
#16/32	0.022	0.073	0.011	0.037
#26	0.014	0.047	0.0070	0.023
#25	0.012	0.040	0.0060	0.020
#28/31	0.040	0.13	0.020	0.070
#33	0.015	0.050	0.0075	0.025
#53	0.0080	0.027	0.0040	0.013
#51	0.0070	0.023	0.0035	0.012
#22	0.022	0.073	0.011	0.037
#45	0.0090	0.030	0.0045	0.015
#46	0.0090	0.030	0.0045	0.015
#52	0.015	0.050	0.0075	0.025
#49	0.010	0.033	0.0050	0.017
#47/48	0.018	0.060	0.0090	0.030
#44	0.013	0.043	0.0065	0.022
#37/42	0.020	0.067	0.010	0.033
#41/71/64	0.020	0.067	0.010	0.033
#40	0.010	0.033	0.0050	0.017
#63	0.025	0.083	0.012	0.040

BZ # (1)	80 L		160 L	
	LOD (MDL) ng/L	LOQ ng/L	LOD (MDL) ng/L	LOQ ng/L
#74	0.013	0.043	0.0065	0.022
#70/76	0.025	0.083	0.012	0.040

BZ # (1)	80 L		160 L	
	LOD (MDL) ng/L	LOQ ng/L	LOD (MDL) ng/L	LOQ ng/L
#66	0.023	0.076	0.012	0.040
#95	0.012	0.040	0.0060	0.020
#91	0.011	0.037	0.0055	0.018
#56/60	0.016	0.053	0.0080	0.027
#92/84	0.024	0.080	0.012	0.040
#89	0.0060	0.020	0.0030	0.010
#101	0.011	0.037	0.0055	0.018
#99	0.0080	0.027	0.0040	0.013
#83	0.0090	0.030	0.0045	0.015
#97	0.0060	0.020	0.0030	0.010
#87	0.010	0.033	0.0050	0.017
#85	0.011	0.037	0.0055	0.018
#136	0.030	0.10	0.015	0.050
#77/110	0.022	0.073	0.011	0.037
#82	0.0070	0.023	0.0035	0.012
#151	0.010	0.033	0.0050	0.017
#135/144	0.013	0.043	0.0065	0.022
#123/149	0.010	0.033	0.0050	0.017
#118	0.016	0.053	0.0080	0.027
#146	0.011	0.037	0.0055	0.018
#132/153/105	0.020	0.067	0.010	0.033
#141	0.0080	0.027	0.0040	0.013
#137/176	0.013	0.043	0.0065	0.022
#163/138	0.022	0.073	0.011	0.037
#158	0.015	0.050	0.0075	0.025
#178	0.014	0.047	0.0070	0.023
#187/182	0.010	0.033	0.0050	0.017
#183	0.011	0.037	0.0055	0.018
#128	0.0090	0.030	0.0045	0.015
#167	0.012	0.040	0.0060	0.020
#185	0.0070	0.023	0.0035	0.012
#174	0.011	0.037	0.0055	0.018
#177	0.012	0.040	0.0060	0.020
#202/171	0.0080	0.027	0.0040	0.013
#172	0.015	0.050	0.0075	0.025
#180	0.013	0.043	0.0065	0.022
#193	0.015	0.050	0.0075	0.025
#199	0.0090	0.030	0.0045	0.015
#170/190	0.011	0.037	0.0055	0.018
#198	0.015	0.050	0.0075	0.025
#201	0.018	0.060	0.0090	0.030
#203/196	0.028	0.093	0.014	0.047

BZ # (1)	80 L		160 L	
	LOD (MDL) ng/L	LOQ ng/L	LOD (MDL) ng/L	LOQ ng/L
#208/195	0.0080	0.027	0.0040	0.013
#207	0.0070	0.023	0.0035	0.012
#194	0.011	0.037	0.0055	0.018
#206	0.0070	0.023	0.0035	0.012

1.3 Pesticide LODs and LOQs: 80 L and 160 L Water

Compound	80 L		160 L	
	LOD (MDL) ng/L	LOQ ng/L	LOD (MDL) ng/L	LOQ ng/L
alpha-BHC	0.050	0.16	0.025	0.082
gamma-BHC (Lindane)	0.050	0.16	0.025	0.082
oxychlordane	0.019	0.063	0.010	0.033
gamma-chlordane	0.022	0.073	0.011	0.037
alpha-chlordane	0.021	0.070	0.010	0.033
trans-nonachlor	0.017	0.057	0.0085	0.028
p,p'DDD	0.050	0.16	0.025	0.082
cis-nonachlor	0.021	0.070	0.010	0.033
p,p'DDT	0.050	0.16	0.025	0.082
toxaphene	10.0	33.0	5.0	16.0
hexachlorobenzene (HCB)	0.0060	0.020	0.0030	0.010
p,p'DDE	0.030	0.10	0.015	0.050

2.0 Sampling

2.1 Water samples are filtered and pumped through XAD-2 resin columns in the field. (See the field standard operating plan.)

2.2 Foil-wrapped filters and resin columns received in the lab from the field are refrigerated at about 4°C until time for laboratory extraction.

3.0 Reagents

3.1 Hexane, acetone, ethyl ether, methylene chloride, methanol - Pesticide Grade

3.2 Sodium sulfate ACS granular; stored at 130°C.

3.3 Silica Gel - Davison Grade 923, 100-200 mesh activated at 130°C, deactivated with 3.5% water for an hour prior to use.

3.4 Florisil - PR Grade 60-100 mesh. Dried at 130°C, stored in air tight container at room temperature.

3.5 Glass wool - Soxhlet extracted in acetone/hexane 50:50 for eight hours.

3.6 Glass fiber filters: 293 mm diameter, 0.7 micron mesh from Microfiltration system, Dublin, CA; wrapped in aluminum foil and heated for four hours at 450°C, stored and sent to the field in the foil packets.

3.7 Resin columns: 5.0 cm X 30.0 cm glass chromatographic columns, with threaded ends, 50 mm thread size; heated for four hours at 450°C.

3.8 Nylon plugs, two per column, 50 mm thread size, and nylon adaptor plugs with swagelock fittings; soaked overnight in a 50/50 mixture of acetone/hexane prior to use. O-rings are soaked in hexane overnight.

3.9 Amberlite XAD-2, 20-60 mesh, Sigma Chemical Company, cleaned as described below.

3.10 HCl-Reagent grade, diluted to 50% and extracted with hexane three times.

4.0 XAD-2 Resin Column Preparation

4.1 The XAD-2 resin is cleaned in the lab by a series of solvent extractions in a large Soxhlet apparatus. Approximately 2.5 kg of resin is extracted sequentially for 24 hrs each in methanol, acetone, hexane, and methylene chloride. This is followed by sequential six hour extractions in acetone, hexane, and acetone. This sequence cycles the resin back to a water-miscible solvent, which is displaced from the resin by rinsing with several volumes of organic free water. Cleaned resin is stored under organic free water in amber bottles for one to three months, until column preparation. The hexane from the 6 hour extraction is used as a resin quality control blank. The final six hour acetone extract can be used as the first acetone on the next batch of resin.

4.2 XAD-2 resin columns are prepared by first attaching one nylon adaptor with a Swagelock fitting and a 3" length of latex tubing to one end of the glass column, and pushing a large plug of cleaned glass wool into the bottom. The column is filled about ½ full with organic free water and clean resin is poured into the column in a slurry to a final packed length of 19.5 cm (400 mL). The resin is packed by pumping excess water out from the bottom using a water aspirator or peristaltic pump but maintaining enough water in the column to cover the resin. The column should not contain air bubbles or channels. The top of the column is plugged with wet glass wool and a nylon plug. The nylon adaptor at the bottom is replaced with a nylon plug. Columns are wrapped for shipping and stored in the lab until picked up by United States Geological Survey sampling crews.

4.3 A log is kept of resin batches as they are being cleaned, and of columns as they are prepared and sent to the field so that traceability of samples to individual columns and to batches of cleaned resin is maintained.

5.0 Surrogate and Matrix Spikes

5.1 Surrogate standards are added to each sample and blank prior to extraction to monitor analytical recoveries of PCB congeners. The surrogates are PCB congeners #14, #65, and #166 at nominal

concentrations of 20, 5, and 5 ng/mL respectively. They are added to the Soxhlet extractor of every sample and blank at the beginning of the analytical procedure.

5.2 The matrix spike solution consists of the following Aroclor mixture: Aroclors 1232, 1248, and 1262 at 0.25, 0.18, and 0.18 mg/L, respectively, in acetone. It does not contain internal standards. With each batch of samples analyzed, an appropriate amount of this spike solution is added by Class A volumetric pipet to a Soxhlet containing clean resin and to a Soxhlet containing a clean filter. Surrogates are also added. These spikes are extracted and analyzed along with the samples.

5.3 With each batch of samples, a separate spike of chlorinated pesticides is added to a Soxhlet containing clean resin and to a Soxhlet containing a clean filter.

6.0 Sample Extraction - Resin and Filters

6.1 The resin, representing the dissolved portion of a surface water sample, is analyzed by extracting the resin and glass wool plugs in two Soxhlets, each with a 500 mL mixture of 50% acetone/50% hexane, for 16 hours. Excess water at the top of the resin column is first poured off into an Erlenmeyer flask. Resin is transferred to the Soxhlets in an acetone slurry, and rinsed at least twice with acetone to remove as much water as possible. This acetone-water "rinsate" (400 to 450 mL) is added to the water in the Erlenmeyer and set aside. Surrogate spike solution is added to each resin Soxhlet and to the rinsate.

6.2 The Soxhlet extract will still contain some water which will result in a two-layer acetone-and-water/hexane system. After extraction is complete, the extract is reduced in volume on a rotary evaporator to approximately 300 mL and transferred to a 500 mL separatory funnel. The water layer is drawn off and combined with the rinsate from that sample in a 1 L or 2 L separatory funnel. The hexane layer is saved. Then 300 mL of organic-free water is added to the rinsate. Five (5) mL of 50% HCl is added to minimize emulsion. The rinsate is then extracted three times with 100 mL, 75 mL and 75 mL of hexane. The hexane extracts are combined with the hexane layer from the Soxhlet extract and concentrated to approximately 5 mL using 15 mL of iso-octane as a keeper. Sodium sulfate (approximately 10g) is added to absorb residual water.

6.3 Filters from each sample are combined and extracted in a Soxhlet (separately from the resin) with a 600 mL mixture of 50% acetone/50% hexane for 16 hours. Surrogate spike is added to the Soxhlet at the beginning of the extraction.

6.4 The filter extract also contains some water which will form a separate layer. The filter extract is concentrated to approximately 300 mL on a rotary evaporator, and transferred to a 500 mL separatory funnel. The water layer is drawn off, transferred to a second separatory funnel, and 100 mL of organic-free water is added. Five (5) mL of 50% HCl is added to minimize emulsion. The rinsate is then extracted three times with hexane (75 mL, 50 mL, 50 mL). The hexane extracts are combined with the filter Soxhlet hexane layer and concentrated on a rotary evaporator to approximately 5 mL for clean-up, using 15 mL of iso-octane as a keeper. Sodium sulfate (approximately 10g) is added to absorb residual water.

7.0 Sample Clean-up and Fractionation

7.1 Florisil and silica gel column chromatography are employed as clean-up techniques prior to GC-EC analysis. The fractionations are required to separate PCBs from as many other parameters

as possible. This facilitates identification and analysis by GC-EC. The florisil procedure is performed first, followed by silica gel.

7.2 Florisil columns are prepared by placing 1 cm of anhydrous sodium sulfate in a 1 cm i.d. X 30 cm chromatography column fitted with a 75 mL reservoir. The column should be previously filled to slightly above the reservoir base with hexane. Eight grams of 60/100 mesh Florisil (Floridin Company), activated at 130°C for 16 hours, is then added and topped with another 1 cm layer of sodium sulfate. Avoid entrapping air bubbles when pouring the column. Adjust the hexane level to within a few mm of the top layer of sulfate and discard the excess solvent (this also serves as a column wash).

7.3 When hexane reaches the top of the upper sodium sulfate layer, the sample extract is quantitatively transferred to the column and allowed to drain onto the bed of Florisil. The sample container is washed with 5 mL of hexane and added to the column as the original extract has just reached the top layer of sulfate. This also serves to wash down the walls of the column. When the hexane rinse reaches the top of the Florisil, the elution solvent is added, and the eluate is collected for further separation. The volume and makeup of the elution solvent is determined from the Florisil elution check. Currently 50 mL of 94/6 hexane/ethyl-ether is used. This eluate is concentrated under a gentle stream of air to about 5 mL and cleaned up on silica gel. See Section 7.4

7.4 The eluate from the Florisil column must be further fractionated through silica gel to separate PCBs and chlorinated pesticides. Prepare the silica gel by heating at 130°C overnight and deactivating before use by equilibrating one hour with 3.5% distilled water. (The percentage of deactivation may change with different lots of silica gel.) Prepare silica gel columns (1cm i.d. x 30 cm) by first filling with hexane. Add 1 cm of anhydrous sodium sulfate, 5 gm of deactivated silica gel and another 1 cm of sodium sulfate layer and quantitatively add the first florisil fraction. Start collecting the eluate and elute the PCBs, HCB, and p,p'DDE with 50 mL of hexane. Two to 3 mL of iso-octane is added to this SG1 fraction, and it is concentrated down under a gentle stream of air to approximately 5 mL, then transferred to a centrifuge tube and further concentrated to 1.0 mL for GC analysis. A final clean-up is done by adding 1.0 mL concentrated sulfuric acid to the SG1 extract.

7.5 A second fraction is eluted from the silica gel column using 60 mL of 25% ethyl ether in hexane. This will contain alpha-BHC, lindane, the chlordanes, nonachlors, p,p'DDD, p,p'DDT and toxaphene. Two to 3 mL of iso-octane is added to this SG2 fraction and it is concentrated as in Section 7.4 above, transferred to a centrifuge tube and further concentrated to 1.0 mL. A final clean-up of this fraction is done by adding 1 mL of concentrated sulfuric acid to the extract, mixing thoroughly, and allowing to sit for up to 24 hours.

8.0 Gas Chromatography for PCB Congeners, HCB, and p,p'DDE

8.1 GC Conditions

HP 5890-II Gas Chromatograph
60M DB5 column, 0.2 mm ID, 0.1 um film
Hydrogen carrier gas
Electron Capture Detector; 300°C
Pressure Programmable Injector; 265°C

Initial Pressure 40 psi, 1.0 min hold
Programmed from 40 psi to 20 psi at 20 psi/min, then go to constant flow mode for remainder of run
Splitless injection; purge on at 0.70 min
Injector volume 1 µL
Oven Temperature Profile:
Initial Temp 100°C, hold for 1.0 min
100°C to 150°C at 3°C/min
150°C to 220°C at 1°C/min
220 C to 280 C at 5°C/min, hold for three min

8.2 Standards

The single point calibration standard consists of a dilution of a stock solution of Aroclors 1232, 1248,and 1262 at 183 μg/mL which was supplied by M. Mullein in June 1994. See Table 1293.8b1 for congener composition of the stock solution. The diluted standard contains Aroclors 1232, 1248, and 1262 at .225, .162, and .162 ng/L for a total of .549 μg/mL PCB. Quantitation of congeners #128 and #167 requires the addition of individual standards of these congeners to the calibration mix, at nominal concentrations of 4 ng/mL and 2 ng/mL, respectively. The total concentration of these congeners in the calibration mix must also include the contribution from the Aroclors. This contribution is 0.30 ng/mL of #128 and 0.15 ng/mL of #167. This standard also contains PCB congener #30 at a nominal concentration of 0.012 mg/L (12. ng/mL), and PCB congener #204 at 0.013 mg/l (13. ng/mL) which are used as retention time reference peaks and as internal standards for quantitation. Congeners eluting prior to and including #77/110 use congener #30 as internal standard, those eluting after #77/110 use congener #204 as internal standard. The calibration table contains the concentration in ng/mL of each congener in the mix, including internal standards, as well as surrogates #14, #65, and #166 at nominal concentrations of 32, 7, and 8 ng/mL. See Table 1293.8b2.

8.3 A three-level calibration is performed yearly to verify detector response linearity, using the single-point standard and standards at 0.5x and at 2x the single point standard. The RSD of the three response factors for each congener shall be less than 25%. Alternatively, linearity may be demonstrated by a correlation coefficient of at least 0.95.

8.4 Pesticide standards containing HCB, trans-nonachlor, and p,p'-DDE at concentrations of 4-8 ng/mL and containing internal standards #30 and #204 are also run with each batch of PCB extracts.

8.5 Instrument Performance

Congener response factors are generated daily from a run of the single point calibration standard. This standard will also be run every 12 hours as a performance standard and evaluated for resolution, reproducibility, and sensitivity. In addition, a PCB performance standard at either the .5x or 2x concentration will be run at a nominal frequency of every other sample batch. The calculated concentrations of congeners #44, #101, #185 and #180 shall not differ from their known concentrations by more than 25%. The calculated concentrations of congeners #6 and #198 shall not differ from their known concentrations by more than 50%. If these limits are exceeded, response factors will be regenerated, or the necessary instrument maintenance will be performed.

8.6 Samples

Some samples may need to be screened by packed column GC-EC. This is to insure that there has been adequate clean-up, and that samples are diluted or concentrated to an appropriate volume for injection onto the capillary column. Exactly known amounts of internal standards are added to the cleaned-up sample extract just prior to capillary column gas chromatography. An appropriate amount (usually 25 µL) of a standard containing congeners #30 and #204 is added to the sample extract to bring their concentrations in the extract to approximately the same as they are in the calibration standard.

8.7 Calculations

Calculations for PCB Congeners are done by the HP3396 Integrator using the formula for internal standard quantitation:

$$Conc. = \frac{Height\ (y)}{Height(IS)} \times \frac{RF\ (y)}{RF(IS)} \times Amount\ (IS) \times Mult.$$

Where: y = analyte
IS = internal standard
RF = response factor = mass/peak ht.
Amount(IS) = mass of internal standard added to the sample
Mult. = multiplier = 1/sample volume

Response factors are generated from a daily run of the calibration standard. Calculations for HCB and p,p'-DDE are done manually using the same internal standard formula, and using congener #30 as internal standard.

8.8 Confirmation

Confirmation of correct PCB and pesticide identification is done on 5% of the SG1 extracts by retention time agreement on a 60M DB-1column, using the same GC conditions and standards as given in Sections 8.1 and 8.2. Table 1293.8h1 contains the concentration in ng/mL of each congener in the mix.

9.0 Gas Chromatography for Pesticides in the Second Silica Gel Fraction

9.1 GC Conditions

HP 5890 Gas Chromatograph or equivalent
60M DB1 column, 0.2 mm i.d., 0.1 um film
Hydrogen carrier gas
Electron Capture Detector
Oven Temperature Profile:
90°C Initial temperature
90°C to 120°C at 10°C/min

120°C to 245°C at 4°C/min
245°C to 280°C at 15°C/min, hold for 6 min
Injector temperature 265°C
Detector temperature 320°C
Pressure Programmable Injector
Initial Pressure 25 psi, 1 min hold
Programmed from 25 psi to 16.5 psi at
10 psi/min, hold at 16.5 psi 42 min
Splitless injection, 1 µL; purge on at 0.80 min

Retention times are given in the following table:

Compound	RT, min.	RRT vs #204
alpha-BHC	15.90	.459
gamma-BHC (lindane)	17.36	.502
#30 (Int. Std)	17.80	.514
oxychlordane	25.08	.725
gamma-chlordane	25.94	.749
alpha-chlordane	26.76	.773
trans-nonachlor	27.20	.786
p,p'DDD	29.57	.854
cis-nonachlor	29.87	.863
p,p'-DDT	31.49	.910
#204 (RT Reference)	34.61	1.000
toxaphene compounds	27 to 36 min.	---

9.2 Standards

A mixed standard containing the chlorinated pesticides at 4 to 8 ng/mL and also containing congeners #30 and #204 as internal standards and retention time reference peaks is run with each set of samples. Standards at 2x or 3x those concentrations will be run if high concentrations are expected in samples. A standard containing toxaphene at 0.80 mg/L is also run with each batch of samples.

9.3 Instrument performance

Response factors for pesticides are generated daily from a run of the 4 to 8 ng/mL standard. This standard, or the 2x or 3x standard, will be run daily as a performance standard.
Calculated concentrations of pesticides in the performance standard should not differ from the known concentration by more than 20%.

9.4 Samples

Internal standards PCB #30 and #204 are added to the second silica gel fraction, which has been cleaned up with sulfuric acid (See Section 7.5), just prior to capillary column gas chromatography.

9.5 Calculations for pesticides

Calculations for pesticides are done using peak heights, and the same internal standard formula given in Section 8.7. PCB congener #30 is used as the internal standard for all pesticides; there is often an interference in this fraction which co-elutes with congener #204.
Note: Trans-nonachlor may split on the silica gel and be found in both fractions. If this occurs it is quantitated in both fractions and the sum is reported.

9.6 Calculations for toxaphene
Toxaphene is a multi-component mixture of chlorinated camphenes. Identification of toxaphene in a sample requires a minimum of five sample peaks matching the retention times of standard peaks. Quantitation is done by summing peak heights of five or more matching peaks in the sample and in the standard, and using the internal standard formula:

$$Conc = \frac{\text{Sum of peak heights (sample)}}{\text{Ht IS (sample)}} \times \frac{RF(y)}{RF(IS)} \times \frac{\text{Amount IS}}{\text{sample vol.}} \times \frac{1}{L}$$

Where y = toxaphene

$$RF(y) = \frac{\text{mass of standard}}{\text{Sum of peak heights (std)}}$$

9.7 Confirmation

Confirmation of SG2 pesticides is done on 5% of the samples by retention time agreement on a second column (e.g. 60M DB-5), or by GC/MS.

10.0 References

10.1 Ballschmiter, K. and Zell, M., 1980. Fresenius Z. Anal. Chem., 302, 20-31.

10.2 M. Mullein, File=C:\QPR04\QC\LMMBPCB1.WQ1 21-June 1994 (Table 1293.8b1).

Table 1293.8b1 PCB Stock Solution Concentrations 183 µg/mL

FILE=C:\QPRO4\QC\LMMBPCB1.WQ1 21-Jun-94 2 Sig.Fig. 15:01 LMMB CALCULATED AVERAGE Calc'd		FILE=C:\QPRO4\QC\LMMBPCB1.WQ1 21-Jun-94 2 Sig.Fig. 15:01 LMMB CALCULATED AVERAGE Calc'd	
Peak Name	**Congener Conc'ns µg/mL**	**Peak Name**	**Congener Conc'ns µg/mL**
PCB-000	4.1	PCB-097	0.56
PCB-001	12	PCB-099	0.74
PCB-003	7.0	PCB-100	0.11

Table 1293.8b1 PCB Stock Solution Concentrations 183 µg/mL

FILE=C:\QPRO4\QC\LMMBPCB1.WQ1 21-Jun-94 2 Sig.Fig. 15:01 LMMB CALCULATED AVERAGE Calc'd		FILE=C:\QPRO4\QC\LMMBPCB1.WQ1 21-Jun-94 2 Sig.Fig. 15:01 LMMB CALCULATED AVERAGE Calc'd	
Peak Name	**Congener Conc'ns µg/mL**	**Peak Name**	**Congener Conc'ns µg/mL**
PCB-004+010 (SUM)	3.4	PCB-101	1.8
PCB-006	1.9	PCB-107	0.13
PCB-007+009 (SUM)	1.2	PCB-110	1.9
PCB-008+005 (SUM)	14	PCB-114+131 (SUM)	0.14
PCB-012	0.17	PCB-118	1.2
PCB-013	0.097	PCB-119	0.028
PCB-015+017 (SUM)	3.7	PCB-123+149 (SUM)	2.8
PCB-016	2.0	PCB-128	0.10
PCB-018	3.7	PCB-129	0.013
PCB-019	0.28	PCB-130	0.075
PCB-021	0.032	PCB-132+153+105 (SUM)	4.3
PCB-022	2.9	PCB-134R	0.072
PCB-024+027 (SUM)	0.26	PCB-135+144 (SUM)	0.89
PCB-025	0.32	PCB-136	0.75
PCB-026	0.72	PCB-137+176 (AVE)	0.26
PCB-029	0.053	PCB-141	1.7
PCB-031+028 (SUM)	9.4	PCB-146	0.39
PCB-032	1.9	PCB-151	1.7
PCB-033	3.3	PCB-156	0.066
PCB-037	1.2	PCB-157+200 (AVE)	0.39
PCB-040	0.94	PCB-158	0.25
PCB-041+071 (AVE)	2.3	PCB-163+138 (SUM)	2.7
PCB-042	1.4	PCB-167	0.049
PCB-043	0.27	PCB-170+190 (SUM)	1.7
PCB-044	4.3	PCB-172	0.56
PCB-045	0.89	PCB-173	0.038
PCB-046	0.40	PCB-174	3.2
PCB-047	1.0	PCB-175	0.20
PCB-048	1.0	PCB-177	1.7
PCB-049	2.3	PCB-178	1.1
PCB-051	0.18	PCB-180	6.1
PCB-052	4.5	PCB-183	1.7

Table 1293.8b1 PCB Stock Solution Concentrations 183 µg/mL

FILE=C:\QPRO4\QC\LMMBPCB1.WQ1 21-Jun-94 2 Sig.Fig. 15:01 LMMB CALCULATED AVERAGE Calc'd		FILE=C:\QPRO4\QC\LMMBPCB1.WQ1 21-Jun-94 2 Sig.Fig. 15:01 LMMB CALCULATED AVERAGE Calc'd	
Peak Name	**Congener Conc'ns µg/mL**	**Peak Name**	**Congener Conc'ns µg/mL**
PCB-053	0.64	PCB-185	0.47
PCB-056+060 (AVE)	3.5	PCB-187+182 (AVE)	3.6
PCB-063	0.21	PCB-189	0.040
PCB-064	1.8	PCB-191	0.12
PCB-066	5.2	PCB-193	0.42
PCB-070+076 (SUM)	3.4	PCB-194	1.8
PCB-074	1.9	PCB-197	0.11
PCB-077	0.23	PCB-198	0.12
PCB-081	0.16	PCB-199	0.43
PCB-082	0.44	PCB-201	4.2
PCB-083	0.15	PCB-202+171 (AVE)	0.79
PCB-085	0.70	PCB-203+196 (SUM)	4.3
PCB-087	1.0	PCB-205	0.11
PCB-089	0.10	PCB-206	0.68
PCB-091	0.51	PCB-207	0.093
PCB-092+084 (SUM)	1.8	PCB-208+195 (SUM)	0.80
PCB-095	2.0	PCB-209	0.012

Table 1293.8b2 PCB Congener Calibration Concentrations - DB-5 Column

CAL #	Name	Amount ng/mL	CAL #	Name	Amount ng/mL
1	#1	3.6000E+01	42	#83	4.5000E-01
2	#3	2.1000E+01	43	#97	1.6800E+00
3	#4/10	1.0200E+01	44	#87	3.0000E+00
4	#7/9	3.6000E+00	45	#85	2.1000E+00
5	#6	5.7000E+00	46	#136	2.2500E+00
6	#8/5	4.2000E+01	47	#77/110	6.4000E+00
7	#14	3.1600E+01	48	#82	1.3200E+00
8	#19	8.4000E-01	49	#151	5.1000E+00
9	ISTD1#30	1.4200E+01	50	#135/144	2.6700E+00
10	#18	1.1100E+01	51	#123/149	8.4000E+00

Table 1293.8b2 PCB Congener Calibration Concentrations - DB-5 Column

CAL #	Name	Amount ng/mL	CAL #	Name	Amount ng/mL
11	#15/17	1.1100E+01	52	#118	3.6000E+00
12	#24/27	7.8000E-01	53	#146	1.1700E+00
13	#16/32	1.1700E+01	54	#132/153/105	1.2900E+01
14	#26	2.1600E+00	55	#141	5.1000E+00
15	#25	9.6000E-01	56	#137/176	7.8000E-01
16	#28/31	2.8200E+01	57	#163/138	8.1000E+00
17	#33	9.9000E+00	58	#158	7.5000E-01
18	#53	1.9200E+00	59	#178	3.3000E+00
19	#51	5.4000E-01	60	#166	8.4000E+00
20	#22	8.7000E+00	61	#187/182	1.0800E+01
21	#45	2.6700E+00	62	#183	5.100E+00
22	#46	1.2000E+00	63	#128	4.3000E+00
23	#52	1.3500E+01	64	#167	1.9000E+00
24	#49	6.9000E+00	65	#185	1.4000E+00
25	#47/48	6.0000E+00	66	#174	9.6000E+00
26	#65	7.8000E+00	67	#177	5.1000E+00
27	#44	1.2900E+01	68	#202/171	2.3700E+00
28	#37/42	7.800E+00	69	#157/200	1.1700E+00
29	#41/71/64	1.2300E+01	70	#ISTD 2 #204	1.5600E+01
30	#40	2.8000E+00	71	#172	1.6800E+00
31	#63	6.3000E-01	72	#180	1.8300E+01
32	#74	5.7000E+00	73	#193	1.2600E+00
33	#70/76	1.0200E+01	74	#199	1.3000E+00
34	#66	1.5600E+01	75	#170/190	5.1000E+00
35	#95	6.0000E+00	76	#198	3.6000E-01
36	#91	1.5300E+00	77	#201	1.3000E+01
37	#56/60	1.0500E+01	78	#203/196	1.3000E+01
38	#92/84	5.4000E+00	79	#208/195	2.4000E+00
39	#89	3.0000E-01	80	#207	2.8000E-01
40	#101	5.4000E+00	81	#194	5.4000E+00
41	#99	2.2200E+00	82	#206	2.0000E+00

Table 1293.8h1 PCB Congener Calibration Concentrations - DB-1 Column

CAL #	Name	Amount ng/mL	CAL #	Name	Amount ng/mL
1	#1	3.6000E+01	44	#97	1.7000E+00

Table 1293.8h1 PCB Congener Calibration Concentrations - DB-1 Column

CAL #	Name	Amount ng/mL	CAL #	Name	Amount ng/mL
2	#3	2.1000E+01	45	#87	3.0000E+00
3	#4/10	1.0000E+01	46	#85	2.1000E+00
4	#7/9	3.6000E+00	47	#136	2.3000E+00
5	#6	5.7000E+00	48	#110	5.7000E+00
6	#8/5	4.2000E+01	49	#82	1.3000E+00
7	#14	3.1600E+01	50	#151	5.1000E+00
8	ISTD1 #30	1.4200E+01	51	#135	8.4000E-01
9	#18	1.1000E+01	52	#144	1.8000E+00
10	#15/17	1.1000E+01	53	#123/149/118	1.2000E+01
11	#24/27	7.8000E-01	54	#105/146/132	5.3000E+00
12	#16	6.0000E+00	56	#153	8.1000E+00
13	#32	5.7000E+00	57	#141	5.1000E+00
14	#26	2.2000E+00	58	#137/130	1.0000E+00
15	#25	9.6000E-01	59	#138/168	8.1000E+00
16	#31	1.4000E+01	60	#158	7.5000E-01
17	#28	1.3000E+01	61	#166	8.4000E+00
18	#33/53	1.1800E+00	62	#178	3.3000E+00
20	#22	8.7000E+00	64	#182/187/128	1.5000E+01
21	#45	2.7000E+00	65	#183	5.1000E+00
22	#46	1.2000E+00	66	#167	1.9000E+00
23	#52	1.3500E+01	67	#185	1.4000E+00
24	#49	6.9000E+00	68	#174	9.6000E+00
25	#48	3.0000E+00	69	#177	5.1000E+00
26	#47	3.0000E+00	70	#171/156	1.5000E+00
27	#65	7.8000E+00	71	#173	1.1000E-01
28	#44	1.3000E+01	72	#200	1.5000E+00
29	#42	4.2000E+00	73	#ISTD 2 #204	1.5600E+01
30	#41/71/64	1.2300E+01	74	#172	1.7000E+00
31	#40	2.8000E+00	76	#180	1.8000E+01
32	#63	6.3000E-01	77	#193	1.3000E+00
33	#74	5.7000E+00	78	#199	1.3000E+00
34	#70/76	1.0000E+01	79	#170	3.6000E+00
35	#66	1.6000E+01	80	#190	1.4000E+00
36	#95	6.0000E+00	81	#198	3.6000E-01
37	#91	1.5000E+00	82	#201	1.3000E+01
38	#56/60	1.0000E+01	83	#203/196	1.3000E+01
39	#84	3.9000E+00	84	#195	2.0000E+00

Table 1293.8h1 PCB Congener Calibration Concentrations - DB-1 Column

CAL #	Name	Amount ng/mL	CAL #	Name	Amount ng/mL
40	#89	3.0000E-01	85	#207	2.8000E-01
41	#101	5.4000E+00	86	#194	5.4000E+00
42	#99	2.2000E+00	88	#206	2.0000E+00
43	#83	4.5000E-01			

Lake Michigan Tributary Study Measurement Quality Objectives

QC Description	PCBs QC Objective	Trans-Nonachlor QC Objective
Holding Time & Storage To extraction After Extraction Storage Conditions	 NA NA 4° C.	 NA NA 4° C.
Sample Set	≤8	≤8
Reporting Units	ng/L Dissolved and Particulate	ng/L Dissolved and Particulate
XAD Cleanliness Check Frequency Criteria	 1 per resin batch <MDL	 1 per resin batch <MDL
Method Detection Limit (MDL) Frequency Criteria Source	 1/year +3sd, n=7 Ultra 10 mix	 1/year +3sd, n=7
System Detection Limit Frequency Criteria	 EPA to calculate	 EPA to calculate
Initial Calibration Levels Frequency Criteria Source	3 point 1/year RF RSD<25% Mullin (1994)	3 point 1/year RF RSD<25%
Continuing Calibration Frequency Criteria Source	1 point daily #101,185,44,180<25% #6,198<50% Mullin (1994)	1 point daily ±20%

Lake Michigan Tributary Study Measurement Quality Objectives

QC Description	PCBs QC Objective	Trans-Nonachlor QC Objective
Blanks		
Field Blanks (FRB)		
Frequency	1:20	1:20
Criteria	<MDL x 3.3	<MDL x 3.3
Lab Reagent Blank (LRB)		
Frequency	1 per set	1 per set
Criteria	<MDL	<MDL
Trip Blank (FTB)		
Frequency	1:20	1:20
Criteria	<MDL	<MDL
Lab Dry/Procedural Blank (LDB)		
Frequency	1:20	1:20
Criteria	<MDL	<MDL
Performance Standard (LPC)	Mullin (1994)	
Frequency	every 12 hours	daily
Criteria	#101,185,44,180<25% #6,198<50%	±20%
Surrogate Standards (LSS)	#14,65,166	None to date
Frequency	all samples	
Criteria	50-130%	
Matrix Spike Standards (LMS)		
Frequency	1/set	1/set
Criteria	mean of all congeners: 50-125%	50-120%
Source	Mullin (1994)	
Internal Standards	#30, 204	#30
Frequency	every sample	every sample
Criteria	none	none
Duplicates Field (FDI)		
Frequency	1:20	1:20
Criteria	RPD<100% for conc <5xMDL RPD<50% for conc>5xMDL	RPD<100% for conc<5x MDL RPD<50% for conc>5x MDL
Confirmation (CON)	5% by DB-1 GC/EC	5% by DB-5 GC/EC